Nobel Optical Properties of Conducting Polymer/Nano-structured ZnO System

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新機能有機・無機ナノ複合エレクトロニクス オプトエレクトロニクスデバイスの提言 II

導電性高分子/ナノ構造 ZnO 複合体の光学的性質

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Abstract

Quenching of photoluminescence of conducting polymer and enhancement of photoluminescence of ZnO nano-particles were observed in conducting polymer/ZnO nano-particle system, which is discussed in terms of electron transfer and excited state energy transfer between conducting polymer and ZnO nano-particles.

Key Words: Conducting Polymer, ZnO, Nano-particle, Photoluminescence, Quenching, Electron transfer, Energy transfer

アブストラクト

導電性高分子/ZnO ナノ粒子複合体において導電性高分子の蛍光の消光と ZnO の蛍光の増強が見出され、光励起された導電性高分子と ZnO ナノ粒子の間の電子移動とエネルギー移動を考慮に入れて説明された。

キーワード

導電性高分子、ZnO、ナノ粒子、蛍光消光、蛍光増強、電子移動、エネルギー移動

1. Introduction

Development of organic solar cells based on conducting polymer/C_{60} is triggered by the discovery of photoluminescence quenching and photoconduction enhancement in conducting polymer doped with C_{60} depending on concentration of C_{60}[1)2)]. In these conducting polymer/C_{60} type of solar cells conversion efficiency of more than 3% can be relatively easily realized[3)]. Among various trials of modification of devices[4)], the effect of the introduction of ZnO as transparent cathode has been reported by us[5)]. On the other hand, organic-inorganic nano-composites are expected to exhibit novel electrical and optical characteristics which can be used for developments of novel types of functional device[6)].

2. Experimental

Water-soluble poly(p-phenylene vinylene) derivative poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenyl ene)vinylene) (CPMOPPV) whose molecular structure is shown in Fig.1 was prepared by the method reported by us[7)] as follows.

6-(4-methoxyphenyloxy)-hexanoic acid ester was prepared by treating hydroquinone monomethy ether with 1-bromohexanoic acid ethyl ester and sodium methoxide. 6-(4-methokyphenyloxy)-hexanoic acid ester was then chloromethylated by treating with an excess amount of formaldehyde and hydrochloric acid in dioxane. To afford 6-(2,5-bis(chloromethyl)4-methoxyphenyloxy)-hex anoic acid ethylester. The product was purified by recrystalization from n-hexane.

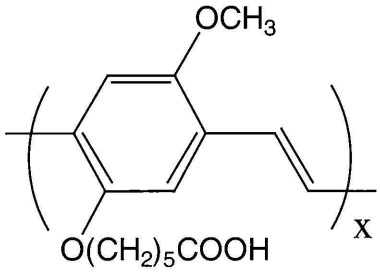


Fig1. Molecular structure of CPMOPPV
図1 CPMOPPV の分子構造

CPMOPPC was prepared by dehydrochlorination polymerization of 6-(2,5-bis(chloromethyl)-4-methokyphenyloxy)-hexanoic acid ethyl ester with potassium tert-butoxide. That is, 2-mthyl-2-propanol solution of potassium *tert*-butoxide was added dropwise to monomer solution with p-xylene and 2-methyl-2-propanol (1:1) at room temperature in an inert atmosphere, and the mixture was refluxed for 24 h. The orange precipitate formed was recovered by filtration, and resolved to be an aqueous solution. Hydrochloric aid was added into the aqueous solution to obtain the orange precipitate of CPMOPPV. The polymer is soluble in common organic solvents, such as acetone, ethanol and tetrahydrofuran. The sodium salt of CPMOPPV, which could be obtained by adding sodium hydroxide (NaOH), is soluble in water.

ZnO nano-particles were prepared by the method already reported[8)]. That is, DC arc discharge method was employed to produce ZnO nano-particles without the use of catalyst. When current is applied between carbon arc and a conducting surface where zinc is placed, the arc gets discharged resulting in high temperature to evaporate zinc from the metallic source and which in turn reacts with

incoming oxygen to produce nano-particles of ZnO. The particles were found to be highly crystalline from the x-ray diffraction pattern. The approximate size of the particles was around 80-100nm. The nano-particles can be dispersed using various solvents such as iso-propanol, ethanol and water by ball mill.

Absorption and photoluminescence were measured at room temperature using a Hewlett Packard HP8452A spectrophotometer and a Hitachi F-2000 spectrophotometer,, respectively.

3. Results and discussion

Figure 2 shows absorption and photoluminescence spectra of CPMOPPV in 2-propanol. As evident in this figure, this polymer exhibits yellow in color and green-glue photoluminescence.

On the other hand, ZnO nano-particles in 2-propanol is color less or pale yellow in color and exhibits ultra-violet photoluminescence as evident in Fig.3.

A solution of ZnO in 2-propanol was mixed with various concentration of CPMOPPV solutions in 2-propanol under ultrasonic irradiation.

As shown in Fig.4, with increasing concentration of CPMOPPV, photoluminescence peak at 360-370 nm originating from ZnO was remarkably reduced. On the other hand, photoluminescence peak at around 510nm originating from CPMOPPV is drastically enhanced. That is, upon increasing concentration of CPMOPPV, photoluminescence from ZnO was quenched and photoluminescence from CPMOPPV was drastically enhanced.

Quenching of photoluminescence of ZnO can be

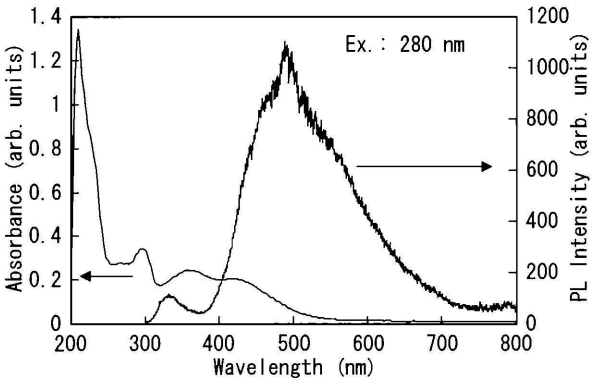


Fig2. Absorption and PL spectra of 2-propanol solution of CPMOPPV
図2 CPMOPPV の2−プロパノール溶液の吸収及び蛍光スペクトル

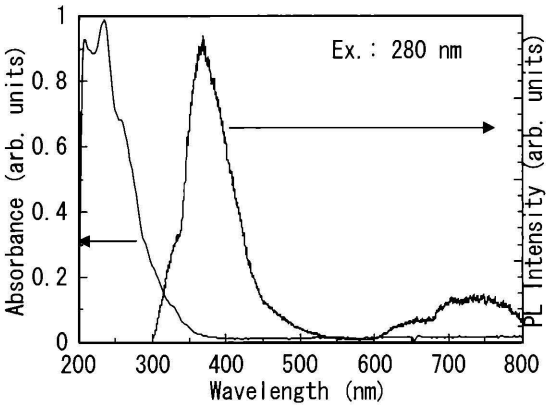
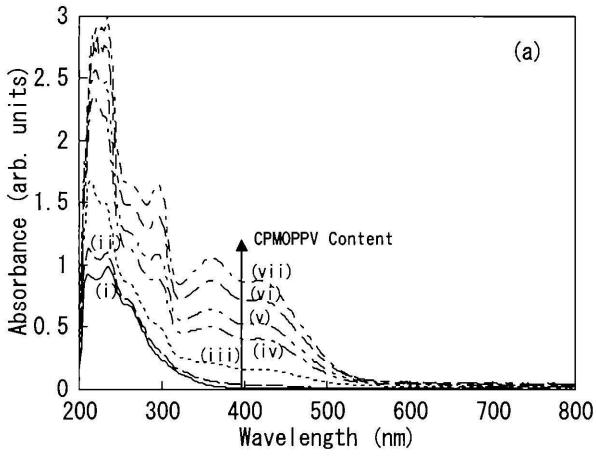


Fig3. Absorption and PL spectra of ZnO nano-particle
図3 ZnO ナノ粒子の吸収及び蛍光スペクトル



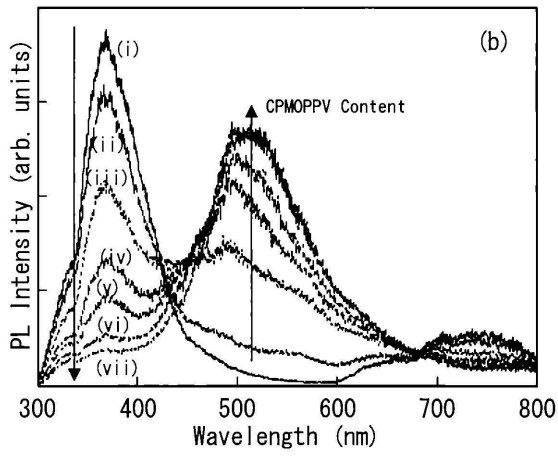


Fig4. Absorption(a) and PL(b) spectra of composites of ZnO nano-particle and CPMOPPV
図4 ZnO ナノ粒子／CPMOPPV 複合体の吸収及び蛍光スペクトル

explained either by dissociation of photo-excited exciton in ZnO by electron transfer (or hole transfer) or photo-excited energy transfer from ZnO to CPMOPPV.

The possibility of electron transfer can not be main effect in this case, because in such a case enhancement of photoluminescence in CPMOPPV can not be simply explained. Therefore, in this case, the excited energy transfer from ZnO to CPMOPPV may be major process. However, the electron energy transfer between CPMOPPV and ZnO can not be completely neglected, because in this experiment of photoluminescence measurements, CPMOPPV is also photo-excited. In this respect, the photoluminescence measurement by the excitation of CPMOPPV at around 400nm is also interesting and now under study.

By taking the electronic energy schemes of both ZnO and CPMOPPV this process can be well understood.

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